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Novel Rheological Properties in Polymer-Organoclay Composites

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Introduction: A series of nanocomposites prepared by melt-blending of cloisite[®] organoclays with polyethylene-vinylacetate (PEVA)/neutralized ethylene-methacrylic acid (PEMA) co-polymers were investigated

Methods and Materials: *in situ* SAXS (small-angle X-ray scattering), TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), TEM (transition electron microscopy) and advanced rheological techniques.

Results: SAXS and TEM data proved high degree of clay exfoliation in all tested nanocomposites. In PEMA and in PEVA both melting temperature T_m and bulk crystallinity were not significantly affected by the presence of organoclays indicating that clay particles are predominantly confined to the amorphous phase in the final morphology. Rheological properties above T_m (determined by DSC) were drastically different in PEVA and PEMA nanocomposites. PEVA-clay systems demonstrated solid-like rheological behavior in small-strain oscillatory shear experiments, yet they were able to flow under a steady shear which is characteristic of physical cross-linking. Also the addition of organoclays to PEVA caused drastic reduction in apparent flow activation energy E_a . In contrast, PEMA-clay composites always exhibited melt-like rheological behavior, E_a variation with clay content in PEMA systems was insignificant. TGA results showed higher thermal stability in all tested composites as compared to the pure polymers. The increase in degradation temperature was more pronounced in PEVA than in PEMA. Furthermore, it was found that surfactant component in organoclays undergoes melting-like transition in the temperature range 35-50 °C, evidenced by broad DSC endotherms and a strong change in SAXS patterns.

Conclusions: We propose that carbonyl groups of vinylacetate interact with hydroxyls present on the clay surface resulting in strong physical cross-linking in PEVA-based materials. On the other hand the interaction between PEMA and clay is weak due to the repulsion between carboxyl anions and negatively charged clay surface, so the physical cross-linking does not occur in PEMA composites.

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